Lattice dynamics of the high-entropy $Zn_{1-x}Mn_xTe$ magnetic semiconductor alloy – Inelastic light/neutron scattering

Due to their simple structure (two bond species randomly arranged on a cubic lattice), the zincblende $A_{1-x}B_xC$ semiconductor alloys (SCA) set a benchmark to explore how physical properties are impacted by disorder. In particular, the vibrational properties governed by the bond force constant potentially offer a suitable probe at the ultimate atom scale (where the atom substitution occurs). A longstanding controversy since the emergence of SCA in the 1960s was whether the vibration of a given bond is "blind" to the alloy disorder, *i.e.*, generates a unique mode at any composition (like in the AC and BC compounds), or actually "sees" the alloy disorder, *i.e.*, diversifies into a multi-mode signal (to clarify in terms of number and nature of modes) reflecting inherent fluctuations in the alloy composition at the local scale. Over the past decade and half our group introduced the percolation model (PM)[1] that distinguishes between like bonds depending on whether they vibrate in "same" or "alien" environments. The PM has been tested and validated on the phonon and phonon-polaritons of various well-matched/WM and highly-mismatched/HM SCA, hence, solving the controversy in favor of the second scenario, apparently.

In this PhD-project we shift the focus from the now well-understood WM/HM-SCA to tackle the magnetic $Zn_{1-x}Mn_x$-SCA (with Mn as the magnetic species), using $Zn_{1-x}Mn_xTe$ as a case study.[2,3] High-quality large-size free-standing $Zn_{1-x}Mn_xTe$ single crystals will be grown specially for the project over a large x-domain ($x \leq 0.8$) by the Bridgman method.[4]

Regarding <u>phonons</u>, the 3d orbital hybridizes into the tetrahedral Mn-bonds but not in Zn-bonds – because the 3d electrons are less tightly bound in Mn than in Zn. This fragilizes the crystal structure of $Zn_{1-x}Mn_x$-based M-SCA,[4] exalting the vibrational properties and possibly leading to an "exotic" phonon behavior. In fact, the Raman signal of $Zn_{1-x}Mn_xTe$ is assigned in terms of the rare intermediary (hence undetermined) type in the historical classification of the phonon mode behavior of SCA.[2,3,5] This might reflect a lack of understanding, which stimulates a careful re-examination within the PM. As for the <u>phonon-polaritons</u> of $Zn_{1-x}Mn_xTe$, they remain unexplored. ZnTe-based SCA exhibit a large band gap and hence are transparent to the visible laser excitation. This offers a chance to study their phonon-polaritons by forward Raman scattering (schematically operating in "transmission"). Last, large Mn incorporation might generate a collective magnetic excitation, *i.e.*, a <u>magnon</u>, likely to be detected by Raman (as observed with $Cd_{1-x}Mn_xTe$[6]) as well as neutron (as observed with MnTe[7]) scattering.

Generally, our ambition is to achieve a coherent fundamental study of the collective dynamic excitations (phonons, phonon-polaritons, magnon) of $Zn_{1-x}Mn_xTe$ throughout the entire Brillouin zone, *i.e.*, from the zone-center phonon-polaritons up to the zone-edge phonons/magnon, by combining inelastic light (Raman) scattering and inelastic neutron scattering, with high-pressure Raman/X-ray-diffraction (using a diamond anvil cell) and *ab initio* phonon calculations in support.

The PhD student will be at the center of the project taking place within the wall-less international laboratory ViSA-IRP (**Vi**brations of **S**emiconductor **A**lloys – **I**nternational **R**elationship **P**roject, 2024 - 2028) funded by the LUE (Lorraine University of Excellence) program. She/he will be directly involved/in charge of the crystal growth (Toruń, Poland), in (high-pressure) Raman measurements (Metz) and in all measurements done on national facilities, to be done in collaboration: high-pressure X-ray diffraction (using the SOLEIL or ESRF synchrotron sources, France) and inelastic neutron scattering (using the ILL neutron reactor – France) – the access to national-size facilities being conditioned to proposal acceptance. Though the PhD project is mostly experimental in nature, the student will also be involved in *ab initio* phonon calculations (SIESTA code,[8] Metz) coming in support of the discussion of all vibrational data.

<u>References:</u> [1]Pagès *et al.* Phys ; Rev. B 77, 125208 (2008); [2]Peterson *et al.*, Phys. Rev. B **33**, 1160 (1986); [3]Talwar *et al.*, Materials Chemistry and Physics **220**, 460 (2018); [4]Strzałkowski *et al.*, Materials **16**, 3945 (2023); [5]Oles *et al.*, J. Phys. C: Solid State Phys. **18**, 6289 (1985); [6]Venugopalan *et al.*, Phys. Rev. B **25**, 2681 (1982); [7]Szuskiewicz *et al.*, Phys. Stat. Sol. C **3**, 1141 (2005); [8]Garcia *et al.*, J. Chem. Phys. **512**, 204108 (2020).

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ViSA-IRP International consortium / 4-years (2024 – 28):
Web site: https://lcp-a2mc.univ-lorraine.fr/projets-de-recherche/ViSA-IRP

PL – Toruń: Crystal growth (Prof. Strzałkowski & Mme Marasek)
PL – Warsaw: X-ray diffraction (Prof. Paszkowicz & Dr. Minikayev)
IN – Mumbai: Inelastic neutron scattering (Dr. Rao)
FR – Paris: High-pressure X-ray diffraction (Dr. Polian)
High-pressure/low-temperature Raman scattering (Dr. Polian)
PT – Aveiro : *Ab initio* (AIMPRO) Raman calculations, Prof. Torres)
FR – Nancy: Solid State Nuclear Magnetic Resonance (Dr. Gardiennet & Dr. Kervern)
FR – Metz : Spectroscopic ellipsometry (Prof. En Naciri & Dr. Broch)
FR – Metz : High-pressure Raman scattering (Prof. Pagès & M. Franchetti)
Ab initio (SIESTA) phonon calculations (Prof. Postnikov)
Percolation model (Prof. Pagès)

PhD-LUE (ViSA – IRP) thesis :
- This PhD-LUE project will be conducted so as to offer the possibility of a double degree, to be obtained both in Metz and Toruń. In this line, the PhD student (hosted in Metz) will spend around 6 months over the three years of the PhD thesis in Toruń (for crystal growth & structure analysis).
- LUE (Lorraine Université Excellence) PhD grant: circa. 1500 € net salary per month over 36 months.

Web site of the Doctoral School (C2MP, Lorraine University) where candidates can apply :
http://doctorat.univ-lorraine.fr/fr/les-ecoles-doctorales/c2mp/offres-de-these